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### Version of attached file:

Published Version

### Peer-review status of attached file:

Peer-reviewed

### Citation for published item:

Savage, Paul S. and Moynier, F. and Chen, H. and Shofner, G. and Siebert, J. and Badro, J. and Puchtel, I.S. (2015) 'Copper isotope evidence for large-scale sulphide fractionation during Earth's differentiation.', *Geochemical perspectives letters*, 1 (1). pp. 53-64.

### Further information on publisher's website:

<http://dx.doi.org/10.7185/geochemlet.1506>

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Letter

The budget of light elements in Earth's core is a long-standing geochemical problem (Poirier, 1994), as constraining such elements and their abundances can tell us much about the physiochemical conditions of Earth's differentiation. Sulphur is often cited as one such element: cosmochemical estimates suggest that the core contains ~2 wt. % S (Dreibus and Palme, 1996); sulphur in the core is seemingly necessary to explain mantle W and Mo abundances (Wade *et al.*, 2012) and can explain the disparity between the radiometric Pb and W isotope ages of the mantle (Wood and Halliday, 2005). However, recent molecular dynamics estimates suggest S may not be present at all in the core (Badro *et al.*, 2014); also, it is unclear as to whether S entered the core as an iron alloy, or as a discrete sulphide phase (O'Neill, 1991). Further complications stem from the fact that late addition of extra-terrestrial S to the mantle, post-core formation, should overwhelm any pre-existing S (isotope) signature (the "late veneer"; Holzheid *et al.*, 2000; Wang *et al.*, 2013). In an effort to investigate the role of S during Earth's differentiation, we have investigated the Cu isotope compositions of bulk Earth and BSE; this is because Cu is siderophile and strongly chalcophile (~2/3 of Earth's Cu is thought to be in the core; Palme and O'Neill, 2014, McDonough, 2003) but is less volatile than S, so is abundant enough in Earth's mantle to have been largely unaffected by a late veneer.

To begin with, it was necessary to obtain robust Cu isotope compositions for both BSE and bulk Earth. To this end, we measured the Cu isotope composition of 88 extra-terrestrial and terrestrial samples using high precision multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS; see Supplementary Information for methods and data tables) and combined these results with pre-existing literature data.

Choosing samples to constrain the Cu isotope composition of BSE is not trivial, due to the specific behaviour of Cu during mantle melting. The concentration of Cu in a mantle melt is predominantly controlled by the consumption of sulphide phases by such a melt (Lee *et al.*, 2012). If melt fraction remains below ~25 %, residual sulphides should retain Cu, which could potentially give rise to isotopic fractionation. With this in mind, two lithologies were initially chosen to constrain the copper isotopic composition of BSE. The first were komatiites, mantle-derived ultramafic lavas generated by high degrees (>25 %) of mantle melting and typically found in Archaean terrains (Arndt, 2008). In this study, we analysed komatiite samples from two localities; 2.4 Ga Vetreny Belt (Baltic Shield) and 2.7 Ga Belingwe (South Africa). The second were "fertile" orogenic lherzolites from Lanzo (Italy) and Horoman (Japan); that is, samples of the mantle that appear to have undergone little to no melt depletion. These data were augmented by Cu isotope analyses of mid-ocean ridge basalts (MORB), which are typically formed by fairly high (10-15 %) degrees of melting of upper mantle. We also include data from a variety of ocean island basalt samples to investigate the possibility of Cu isotope mantle heterogeneities (see Supplementary Information for all sample information).

## Copper isotope evidence for large-scale sulphide fractionation during Earth's differentiation

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doi: 10.7185/geochemlet.I506

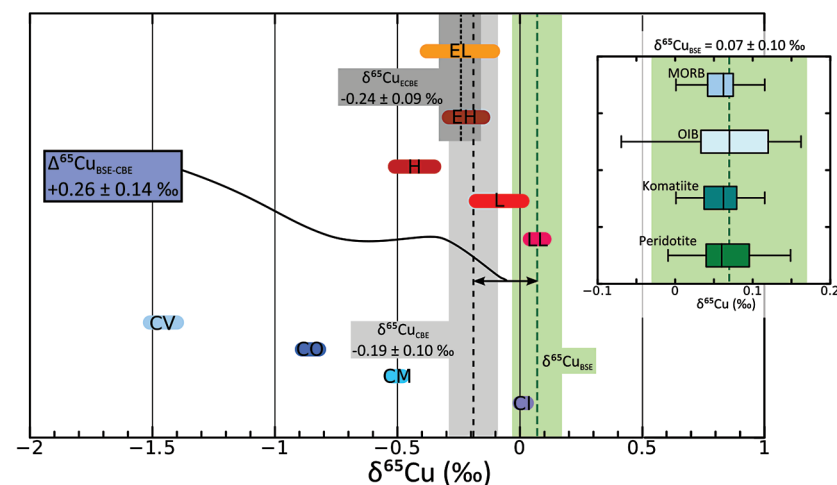
### Abstract

The differentiation of Earth into a metallic core and silicate mantle left its signature on the chemical and isotopic composition of the bulk silicate Earth (BSE). This is seen in the depletion of siderophile (metal-loving) relative to lithophile (rock-loving) elements in Earth's mantle as well as the silicon isotope offset between primitive meteorites (*i.e.* bulk Earth) and BSE, which is generally interpreted as a proof that Si is present in Earth's core. Another putative light element in Earth's core is sulphur; however, estimates of core S abundance vary significantly and, due to its volatile nature, no unequivocal S isotopic signature for core fractionation has thus far been detected. Here we present new high precision isotopic data for Cu, a chalcophile (sulphur-loving) element, which shows that Earth's mantle is isotopically fractionated relative to bulk Earth. Results from high pressure equilibration experiments suggest that the sense of Cu isotopic fractionation between BSE and bulk Earth requires that a sulphide-rich liquid segregated from Earth's mantle during differentiation, which likely entered the core. Such an early-stage removal of a sulphide-rich phase from the mantle presents a possible solution to the long-standing 1<sup>st</sup> terrestrial lead paradox.

Received 18 March 2015 | Accepted 10 April 2015 | Published 4 June 2015

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**Figure 1** Copper isotope range of the primitive (chondritic) meteorite groups. Inset: Box and whisker plot showing the range of Cu isotope compositions for the terrestrial samples used in constraining the BSE Cu isotope composition. Green box and dotted line represents the composition of BSE, light grey box and long dashes represent the composition of “chondritic bulk Earth” (CBE), dark grey box and short dashes represent the composition of “enstatite chondrite bulk Earth” (ECBE). Errors on the estimates are all 2 s.d.

The Cu isotope compositions of terrestrial basalts and ultramafic rocks define a limited range ( $-0.07\text{‰} < \delta^{65}\text{Cu} < +0.16\text{‰}$ ; Fig. 1,  $\delta^{65}\text{Cu} = [({}^{65}\text{Cu}/{}^{63}\text{Cu}_{\text{sample}} / {}^{65}\text{Cu}/{}^{63}\text{Cu}_{\text{std}}) - 1] \times 1000$ ; where std. is NIST SRM976). Despite the potential for Cu isotope fractionation through sulphide retention, each sample group is statistically identical and the data are normally distributed (Supplementary Information), providing a robust and precise average BSE Cu isotope composition of  $\delta^{65}\text{Cu}_{\text{BSE}} = 0.07 \pm 0.10\text{‰}$  (2 s.d.).

It is of course impossible to obtain a sample of the ‘bulk Earth’ and hence, like many studies before ours, we assume that bulk Earth formed from primitive (chondritic) meteorites (e.g., Palme and O’Neill, 2014). The issue then is to decide which group(s) of meteorites best represents Earth, in terms of its Cu budget. This is particularly important, as the range of chondrite Cu isotope compositions span a wide range ( $-1.45\text{‰} < \delta^{65}\text{Cu} < +0.07\text{‰}$ , Fig. 1; Luck *et al.*, 2005), thus we now discuss a number of model-dependent scenarios.

**a) The Earth’s Cu budget was established early in Earth’s accretion:**

Like Cu, large isotope variations also exist in systems such as O, Ti, Cr, Ru, Ca etc., suggesting that no single chondrite group represents a perfect match to Earth, and many workers posit a mixture. Based on modelling of Fitoussi and Bourdon (2012), we calculate a chondritic bulk Earth (CBE) value of  $\delta^{65}\text{Cu}_{\text{CBE}} = -0.19 \pm 0.10\text{‰}$  (2 s.d., Fig. 1). Another approach is to utilise the enstatite chondrites; despite being

chemically dissimilar, these meteorites are identical to the Earth for most isotope systems (Dauphas *et al.*, 2014) and many models suggest that the material that accreted to form the Earth contained a large proportion of enstatite chondrite-like planetesimals (Dauphas *et al.*, 2014). Both enstatite chondrites groups have similar ranges as well as having identical  $\delta^{65}\text{Cu}$  values (Fig. 1); a mixture of EH and EL chondrites gives an enstatite chondrite bulk Earth (ECBE) of  $\delta^{65}\text{Cu} = -0.24 \pm 0.09\text{‰}$  (2 s.d., Fig. 1), identical to  $\delta^{65}\text{Cu}_{\text{CBE}}$ .

**b) The Earth’s Cu was delivered late, as a result of the Moon-forming giant impact:**

The mantle budget of Cu and other moderately volatile elements may be dominated by the final 10 % of material accreted to Earth, associated for example with the Moon-forming giant impactor, Theia (Albarède, 2009). The Cu in the mantle, therefore, would have escaped the effects of all but the final stages of planetary differentiation, as Hf-W isotope data suggests that the majority of the core had formed by the time of impact (Kleine *et al.*, 2010). Work on Ag isotopes by Schönbachler *et al.* (2010) seemed to indicate that the impactor material was dominated by CI-like material. If this is the case, then our data would seem to support their model; our estimate for BSE is almost identical to the Cu isotope composition of CI chondrites. However, more recent isotope data seems to rule out a CI-like impactor; in particular, precise lunar O isotope data suggests that the impactor had an enstatite chondrite isotope signature (Herwartz *et al.*, 2014). In this instance, again, the enstatite chondrite model would seem most representative of bulk Earth.

Accepting either model ‘a’ or ‘b’ above, the bulk Earth Cu isotope composition lies somewhere between  $\delta^{65}\text{Cu} = -0.19 \pm 0.10\text{‰}$  and  $-0.24 \pm 0.09\text{‰}$ . Therefore, in terms of Cu isotopes, BSE is enriched in the heavy Cu isotope compared to bulk Earth, with a minimum offset (taking bulk Earth to be  $-0.19\text{‰}$ ) of  $+0.26 \pm 0.14\text{‰}$  (2 s.d., Fig. 1). This suggests that some process related to planetary differentiation and accretion has affected the Cu isotope composition of Earth’s mantle; we now consider the two most likely culprits: volatile loss of Cu, and core formation.

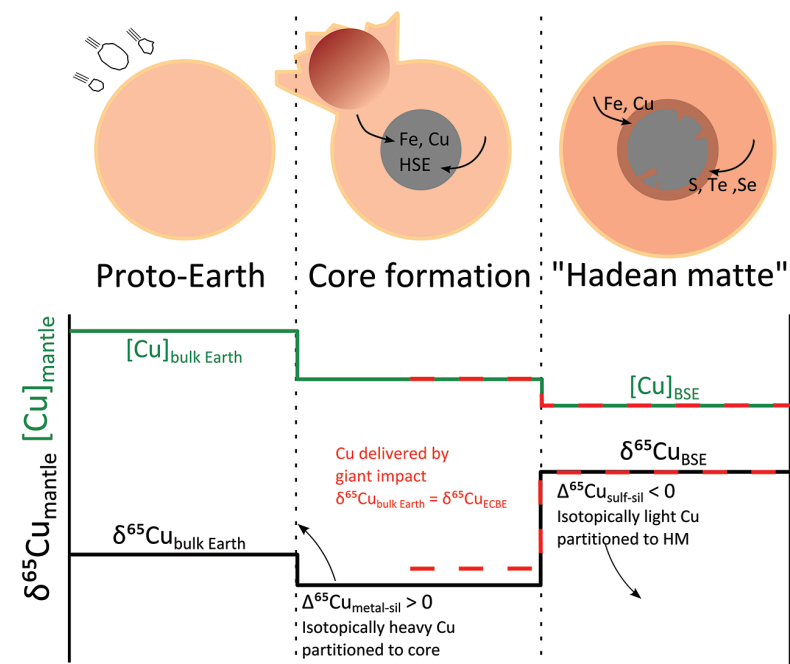
Preferential removal of the lighter Cu isotope during volatile loss could lead to enrichment in isotopically heavy Cu in Earth’s mantle. This, however, can be discounted by considering the Zn isotope system. Zinc is more volatile and less siderophile/chalcophile than Cu (Lodders, 2003); like all moderately volatile, lithophile elements, Earth’s mantle is depleted in Zn compared to most chondrite groups suggesting partial loss or incomplete accretion (Palme and O’Neill, 2014). However, the bulk Earth Zn isotope composition is equal to or lighter than those same meteorites (Albarède, 2009; Chen *et al.*, 2013), *i.e.* contrary to the isotope effect predicted by volatile loss. Hence whichever process(es) resulted in the volatility-related depletion of Zn in Earth’s mantle did not affect its isotopes. It is therefore unlikely that such a process can explain the heavy Cu isotope enrichment in BSE.



Planetary differentiation is therefore the most likely explanation for the Cu isotope difference between BSE and bulk Earth. To further investigate the behaviour of Cu isotopes during core formation, *i.e.* metal-silicate and sulphide-silicate equilibration, we performed a preliminary series of high-pressure, high temperature experiments wherein natural basalt rock powder, doped with Cu (as either metal or oxide) was equilibrated with either pure Fe metal or stoichiometric FeS under fully molten conditions (see Supplementary Information). In the metal-silicate experiments, the direction of isotopic fractionation between the two phases ( $\Delta^{65}\text{Cu}_{\text{metal-silicate}}$ ) was always slightly positive, varying little with temperature ( $\sim +0.1\text{‰}$ ). Crucially, in the sulphide-silicate experiments the sense of fractionation is negative, opposite and with a larger magnitude to that of metal-silicate equilibration ( $> -0.5\text{‰}$ ). These data agree with the sense of Cu isotope fractionation between metal, silicate and sulphide measured in iron meteorites (Williams and Archer, 2011), as well as the extremely light Cu isotope compositions measured in secondary sulphide minerals (Markl *et al.*, 2006). Therefore, the positive Cu isotope difference between BSE and bulk Earth cannot be due to metal-silicate fractionation, because the isotopic fractionation has the incorrect sense. Instead, Earth's "missing" light Cu must be stored in a sulphide-rich reservoir.

Mantle sulphides are a potential explanation; however, given the relative Cu isotope homogeneity of mantle-derived lithologies (Fig. 1) as well as the fact that a typical peridotite contains  $>90\%$  of its Cu in sulphides (Lee *et al.*, 2012), this requires that a relatively significant budget of Cu is stored in sulphides that are never sampled by mantle melting or by tectonic exhumation. This does not seem to be the case: for instance, komatiites, which formed via high degrees of partial melting (such that at least 95 % of the Cu in the mantle source should be transferred to the melt), have Cu isotope compositions equal to that of orogenic lherzolites, which are (arguably) direct samples of the mantle. Komatiites also provide a temporal view on mantle composition and suggest that the Cu isotope composition of BSE was established at least as far back as 2.7 Ga, the age of our oldest sample. Similarly, ocean island basalts, which potentially sample sulphide-rich pyroxenites, show no evidence for significant Cu isotope mantle heterogeneity (Fig. 1). The lower continental crust is also a possible reservoir for isotopically light Cu sulphides – however, even if the bulk Cu concentration in the lower continental crust was three times current estimates, it would only represent  $\sim 0.6\text{ wt. \%}$  of BSE Cu and so would require an unfeasibly light composition ( $\delta^{65}\text{Cu} < -40\text{‰}$ ). Hence, sulphides in the mantle or crust may host some isotopically light Cu, but are apparently not abundant enough to account for the significant Cu isotope offset between BSE and bulk Earth.

An alternative explanation is the early-stage formation of a sulphide-rich (Fe-O-S) liquid in the mantle, as the final volatile-rich residue after crystallisation of a magma ocean; this is often called the "Hadean Matte" (HM; Fig. 2; O'Neill, 1991). Given its higher density compared to ambient mantle, a HM should pond at the core/mantle boundary and, potentially, admix into the core, isolating it from subsequent re-equilibration. Such a reservoir has been invoked to explain



**Figure 2** Schematic evolution of Cu concentration and isotopic composition of Earth's mantle as modelled in this contribution. Earth accretes as a mixture of chondrites such that the bulk Earth Cu isotope composition is  $\delta^{65}\text{Cu}_{\text{CBE}}$ . Core formation sequesters  $\sim 60\%$  of Earth's Cu in the metal phase, which is enriched in the heavy isotope, driving Earth's mantle to a lighter composition. The formation of a Fe-O-S layer, the "Hadean Matte", sequesters isotopically light Cu, driving Earth's mantle to its present day composition ( $\delta^{65}\text{Cu}_{\text{BSE}}$ ). Alternatively, Cu is delivered by an enstatite chondrite-like Giant Impactor, and mantle Cu only experiences sulphide-silicate equilibration.

moderately siderophile element abundances in the mantle (O'Neill, 1991) and the mismatch of various core formation chronometers (Wood and Halliday, 2005), and could host significant amounts of Cu. To this end, we have attempted to calculate the mass and composition of a Hadean Matte needed to balance the Cu isotope offset between BSE and bulk Earth. Following previous models, the HM should form after segregation of the majority (99 %) of the core; as such we have used a simple two-stage model, starting from a chondritic ( $\delta^{65}\text{Cu}_{\text{CBE}}$ ) proto-Earth, where Cu is first partitioned into the core (metal-silicate equilibration), then a sulphide phase (Fig. 2). This is based on model 'a' above, *i.e.* Earth's Cu budget was established early in Earth's accretion. Assuming instead that Earth's mantle Cu was delivered by an enstatite chondrite-like Giant Impactor (model 'b' above) does not significantly change the modelling, except that mantle Cu does not experience major metal-silicate equilibration, only sulphide-silicate equilibration (Fig. 2).

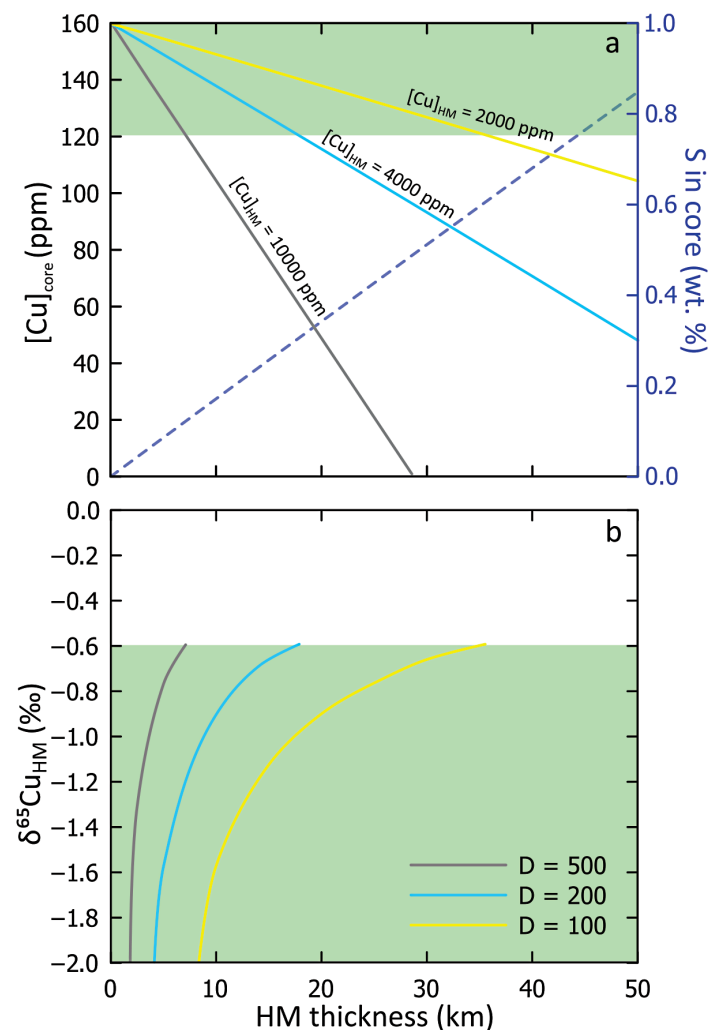


A condition of the model 'a' is that the Cu normally assumed to be in Earth's core is now apportioned between HM and core. Fixing a range of likely Cu concentrations in the HM, we calculated the remaining core [Cu] as a function of HM mass (or thickness, assuming a fixed density). This relationship is shown in Figure 3a, wherein the amount of Cu in the core reduces as the HM thickness and Cu concentration increases. The value of [Cu]<sub>core</sub> should not fall below 120 ppm because Cu is also siderophile (Siebert *et al.*, 2013), which predicts a maximum HM thickness of ~35 km.

We then calculated the Cu isotope composition for each HM scenario required to drive the equilibrating silicate (*i.e.* the mantle) towards the modern-day BSE value. This is shown in Figure 3b, where a smaller HM results in a more negative HM Cu isotope composition. We calculate a range of HM Cu isotope compositions because our preliminary experiments were simply used to assess the sense, not the magnitude of isotope fractionation; however, because large isotope fractionations (> 2 ‰) are not expected at the temperatures associated with the formation of a HM (3000-4000 K), a minimum thickness of ~2 km is predicted, even for the most Cu-rich HM. The maximum size for each HM as controlled by its Cu concentration corresponds to a minimum  $\Delta^{65}\text{Cu}_{\text{sulphide-silicate}}$  value of ~-0.6 ‰. To further constrain this model, further work is required to accurately parameterise Cu isotope fractionation factors, but these model predictions are in general agreement with our experimental data (Supplementary Information).

Admixing a Fe-O-S liquid into Earth's core will affect core composition, specifically with regard to the light elements S and O. Given the constraints provided above (HM mass  $\leq 1.6$  % of Earth's core), addition of a HM to the core will have a small effect on the core O composition (< 0.25 wt. % addition); for S, the effect is more significant – our model suggests that up to ~0.5 wt. % S could be added (Fig. 3a), which is in line with recent estimates based on molecular dynamics (Badro *et al.*, 2014) and siderophile element partitioning studies (Siebert *et al.*, 2013) – of course, this does not preclude further core addition of S as a metal alloy.

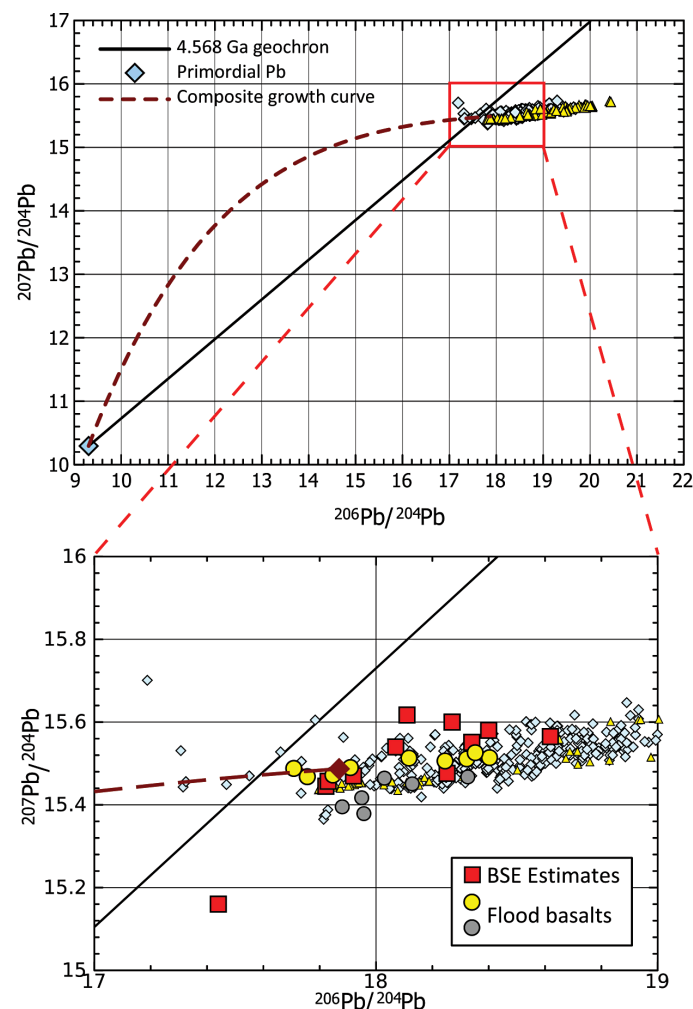
Finally, we estimate the effect that removal of the HM could have on mantle lead isotope composition. Lead can be strongly chalcophile, and an early fractionation of isotopically primitive Pb by a sulphide-rich phase is often cited as a solution to the 1<sup>st</sup> terrestrial Pb paradox; that is, the observation that, in  $^{206}\text{Pb}/^{204}\text{Pb}$  vs.  $^{207}\text{Pb}/^{204}\text{Pb}$  space, most mantle-derived rocks, continental sediments etc. plot to the right of the terrestrial geochron (either the meteoritic, 4.568 Ga geochron or the later Hf-W core formation cessation age of ~4.53 Ga, Fig. 4; Kramers and Tolstikhin, 1997). Modelling the evolution of mantle Pb isotope composition resulting from two fractionation events, metal-silicate equilibration at 50 Ma and sulphide-silicate equilibration at 100 Ma (following Galer and Goldstein, 1996; see Supplementary Information for details), predicts a present-day mantle Pb isotopic composition that is comparable to empirical estimates for BSE, albeit the more unradiogenic ones (Fig. 4; Halliday, 2004) as well as the Pb composition of the ancient primitive mantle as estimated using flood basalts (Jackson and Carlson, 2011). Therefore, this does not preclude further unradiogenic Pb reservoirs, such as sulphides in refractory mantle phases (Burton *et al.*, 2012) or late accretion of mantle Pb (Albarède, 2009).



**Figure 3** Results of modelled effects of removal of a "Hadean Matte" from the mantle. The effects on a) Cu concentration of Earth's core and b) required Cu isotope composition of the HM to produce a modern-day  $\delta^{65}\text{Cu}_{\text{BSE}}$  – plotted as a function of the thickness of the HM. D is the sulphide-silicate Cu partition coefficient. a) Green box defines "allowed" Cu concentrations of Earth's core; [Cu]<sub>core</sub> < 120 ppm do not comply with the siderophile nature of Cu during core formation. Blue dotted line describes the amount of S added to the core (in wt.%) in the case of total mixing of the HM composed of a stoichiometric Fe-O-S liquid into the core. b) Lines plotted here limited to those "allowed" in top panel.







**Figure 4** Modelled evolution of mantle Pb isotope composition as a result of Pb partitioning into the core at 50 Ma and the HM at 100 Ma (composite growth curve). Compilation of mid-ocean ridge basalt (MORB) and ocean island basalt (OIB) data taken from PetDB (<http://www.earthchem.org/petdb>) which all plot to the right (more radiogenic) side of the terrestrial (4.568 Ga) geochron (based on the evolution of Pb from primordial source – based on Canyon Diablo Troilite). Lower figure is a zoom, showing that the composite curve agrees with some of the more unradiogenic estimates for modern day BSE Pb isotope composition (Halliday, 2004), as well as the compositions of certain flood basalt provinces (yellow: Ontong Java Plateau; grey: Baffin Island) thought to best represent ancient primitive mantle composition (Jackson and Carlson, 2011).

To conclude, the Cu isotope composition of BSE seems to require that large scale sulphide-silicate equilibration occurred sometime in Earth's history; here, we have modelled it as the formation of a discreet Fe-O-S reservoir, a “Hadean Matte”, which ponded to the base of the mantle during the final stages of Earth's differentiation. Such a feature likely admixed into Earth's core; however, if any of this material remains, such material could account for recently detected non-chondritic S isotope compositions in Earth's mantle (Labidi *et al.*, 2013). Finally, the Martian core is thought to have up to 14 wt. % S (Wänke and Dreibus, 1994) so FeS-silicate equilibration during core formation could have a significant effect on Mars' mantle; Cu isotopes have the potential to identify this effect.

## Acknowledgements

This research was supported by the Marie Curie IOF Fellowship “Isovolc”, funding from the European Research Council under the European Community's Seventh Framework Programme (FP7/2007-2013)/ERC grant agreement #207467 (DECORE) and under the H2020 framework program/ERC grant agreement #637503 (Pristine), as well as the financial support of the UnivEarthS Labex program at Sorbonne Paris Cité (ANR-10-LABX-0023 and ANR-11-IDEX-0005-02). FM thanks the ANR through a chaire d'excellence Sorbonne Paris Cité and the INSU through the PNP program. ISP acknowledges support from NSF EAR0946629. The authors would like to thank Katharina Lodders, Bruce Fegley, Astrid Holzheid and Kevin Burton for discussions, Juliens Foriel and Moureau for analytical support, and Manuel Moreira, Euan Nisbet, Gary Byerly, Tim Elliott, Fang-Zhen Teng, and Rosalind Helz for sample provision. Three anonymous reviewers and executive editor Graham Pearson greatly improved the text.

Editor: Graham Pearson

## Additional Information

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**Cite this letter as:** Savage, P.S., Moynier, F., Chen, H., Siebert, J., Badro, J., Puchtel, I.S., Shofner, G. (2015) Copper isotope evidence for large-scale sulphide fractionation during Earth's differentiation. *Geochem. Persp. Let.* 1, 53-64.



## Author Contributions

P.S. and F.M. conceived the study and organised sample acquisition, F.M. and H.C. implemented the Cu isotopic analyses and improved the methods, P.S. and H.C. produced all of the Cu isotope data. P.S. produced all of the tables and figures and wrote the majority of the text. G.S., J.S. and J.B. designed and performed the high pressure experiments, performed electron probe analyses and wrote the experimental methods section. I.P. provided the komatiite samples. All of the authors were involved in critiquing the work during its authorship.

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